U.S. Department of Energy's (DOE) Vehicle Technologies Office (VTO)
2022 Annual Merit Review (AMR)

ENABLING CONTINUOUS PRODUCTION OF DEFECT-FREE, ULTRATHIN SULFIDE GLASS ELECTROLYTES FOR NEXT GENERATION SOLID STATE LITHIUM METAL BATTERIES

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PolyPlus Battery Company

Update: April 20, 2022

PROJECT OVERVIEW

Timeline

- Project start: April 8, 2021 (CRADA completed)
- Percent complete: 35%

Budget

- FY21: $83K
- FY22: $166K

Barriers

- Energy density
- Abuse tolerance

Partners

- Argonne National Laboratory
- PolyPlus Battery Company

RELEVANCE

Characterizing the structure and heterogeneity of glass sulfides

- PolyPlus Battery Company has recently installed a draw tower (shown right)that enables the production of ultrathin (<20 μm) glass sulfides.
- This could enable flexible glass electrolytes compatible with roll-to-roll manufacturing.
- **Need: *defect-free* glass.**
  - Defects are related to crystalline inclusions or non-crystalline impurities from glass precursors
  - Defects can arise at the glass surface or at the interface with electrode materials.
  - Origin of defects likely related to immature supply chain for boron/lithium sulfides: need advanced characterization to identify these species in the glass and at localized defects.

APPROACH

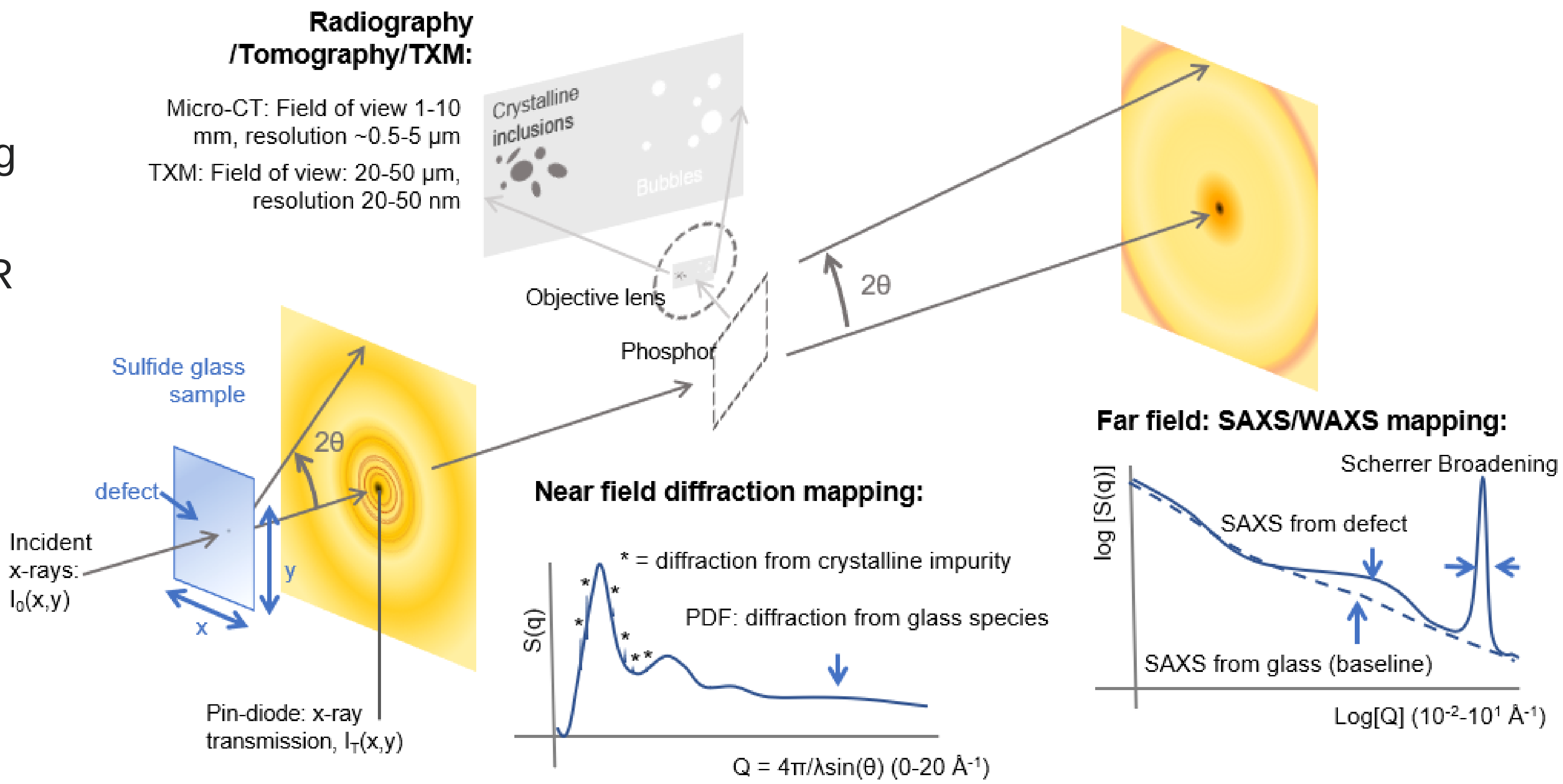
Advanced multimodal characterization at Argonne/APS

Bulk defects:

- Map structure of glass with total x-ray scattering approaches – look for Bragg peaks from impurities.
- Compare with Raman, NMR

Surface/interfacial defects:

- SEM/EDS
- GDOES
- Digital holographic microscopy (DHM)



MILESTONES

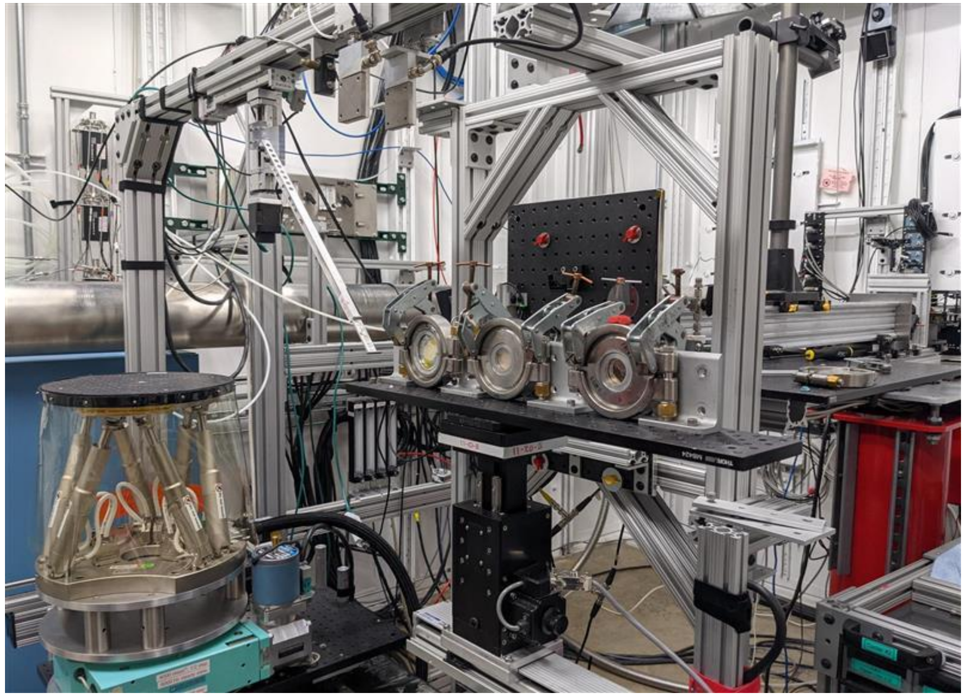
First year

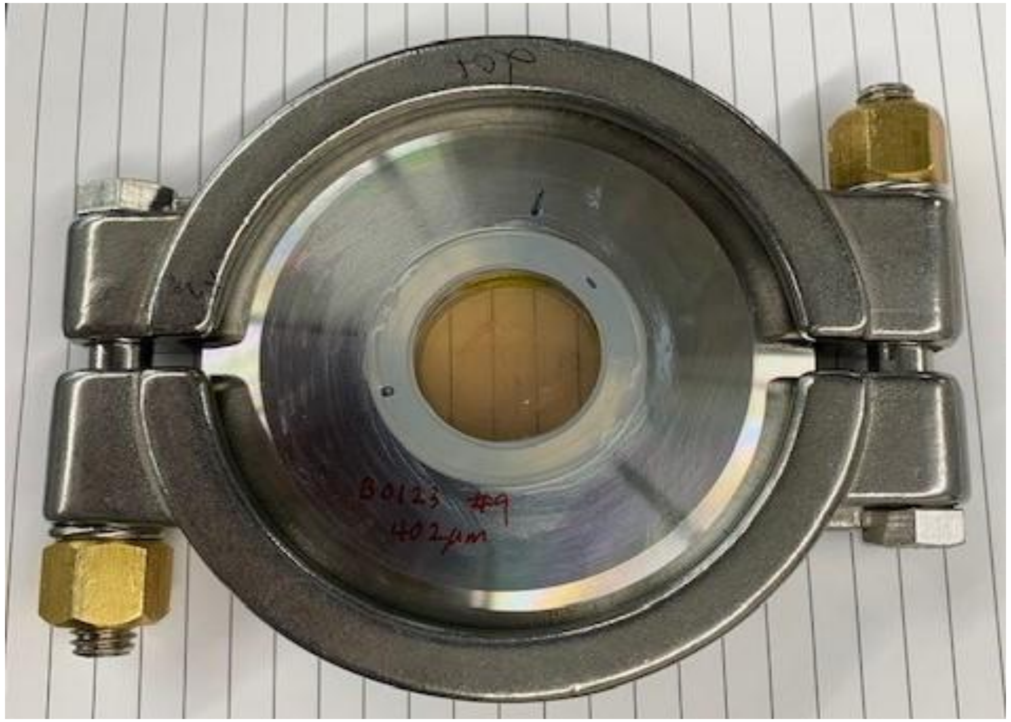
Q1: Identify glass composition range; develop sealed holder for shipment between PolyPlus and ANL/APS.	4/8/21 to 7/8/21	DONE
Q2: Defect Size, distribution: Perform SAXS/WAXS and radiography/TXM on glass samples identified in Q1 (100, 400 µm thick)	7/8/21 to 10/8/21	DONE
Q3: Defect composition: Perform XRD/PDF on glass samples identified in Q1, correlate with Q2 maps and compare defect concentration for thinner samples and samples that have been cycled with Li.	10/8/21 to 1/8/22	DONE
Q4: Task 1 Go/No-Go: Utility of x-ray methods to quantify defects	1/8/22 to 4/8/22	DONE
Q5: Map defects using confocal Raman, compare to Q3 results. Evaluate light scattering methods to analyze defects, compare size with Q2 results.	4/8/22 to 7/8/22	Ongoing

HANDLING SULFIDES

Optical holders for characterization

- Below: sealed holders, developed at PolyPlus, for characterization outside glovebox.
- Also designed transfer vessel for bringing samples/holders through glovebox antechamber.

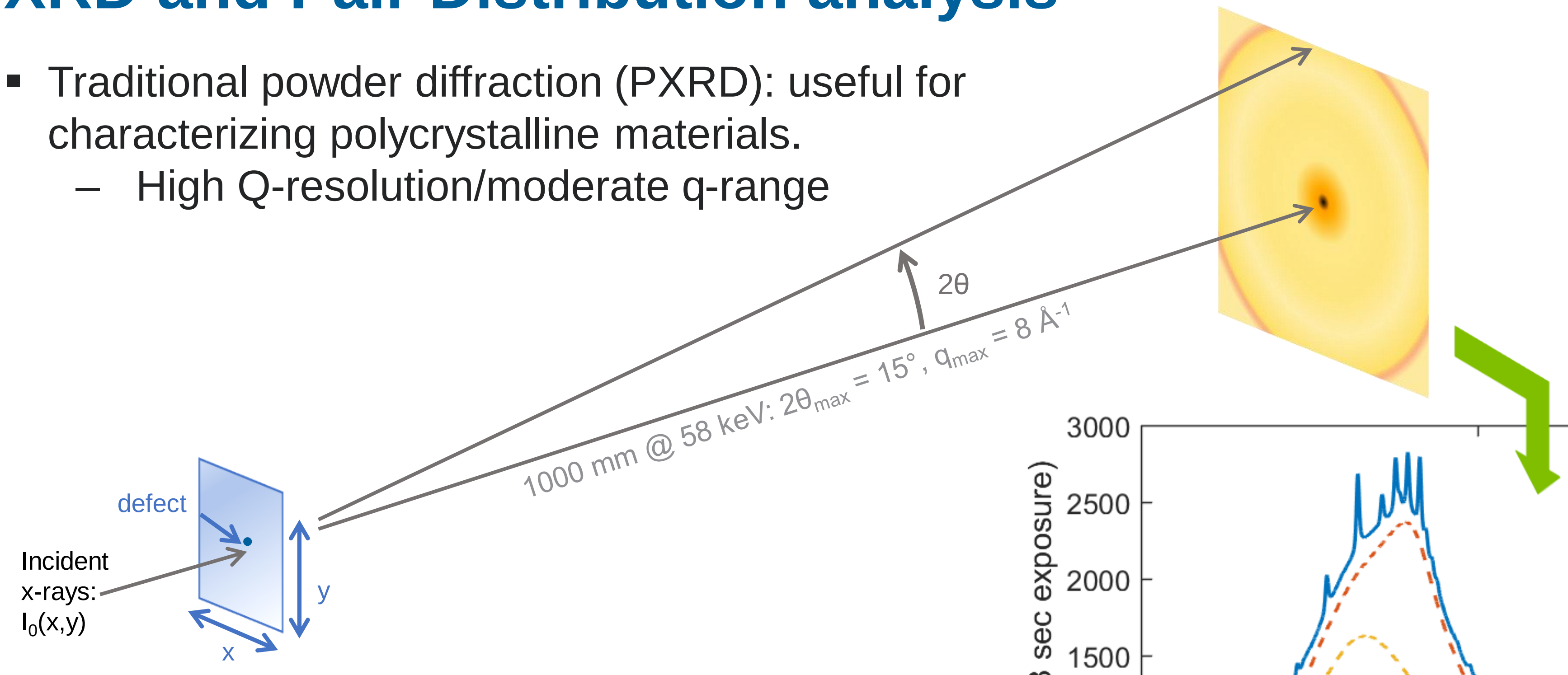


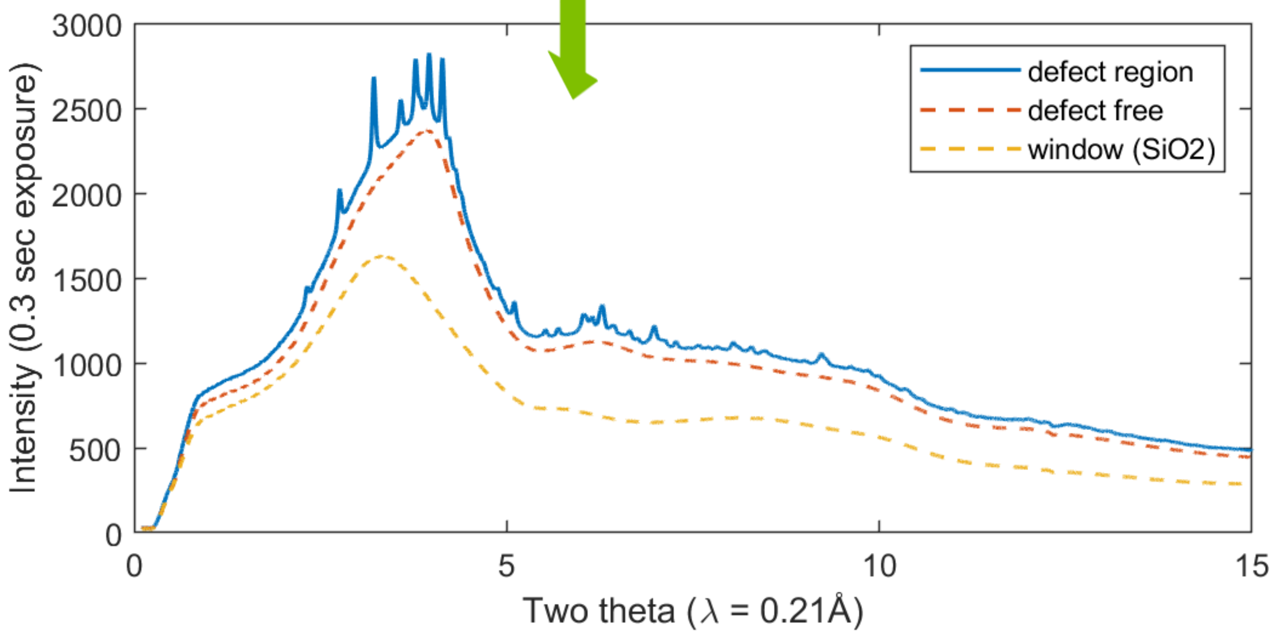


BULK DEFECTS

XRD and Pair Distribution analysis

- Traditional powder diffraction (PXRD): useful for characterizing polycrystalline materials.
  - High Q-resolution/moderate q-range



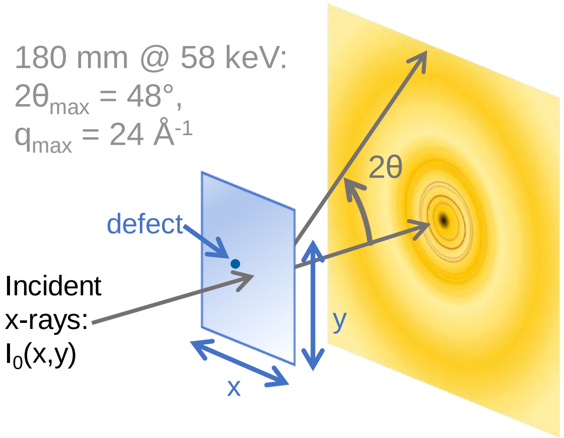


Powder XRD example from sample B0135

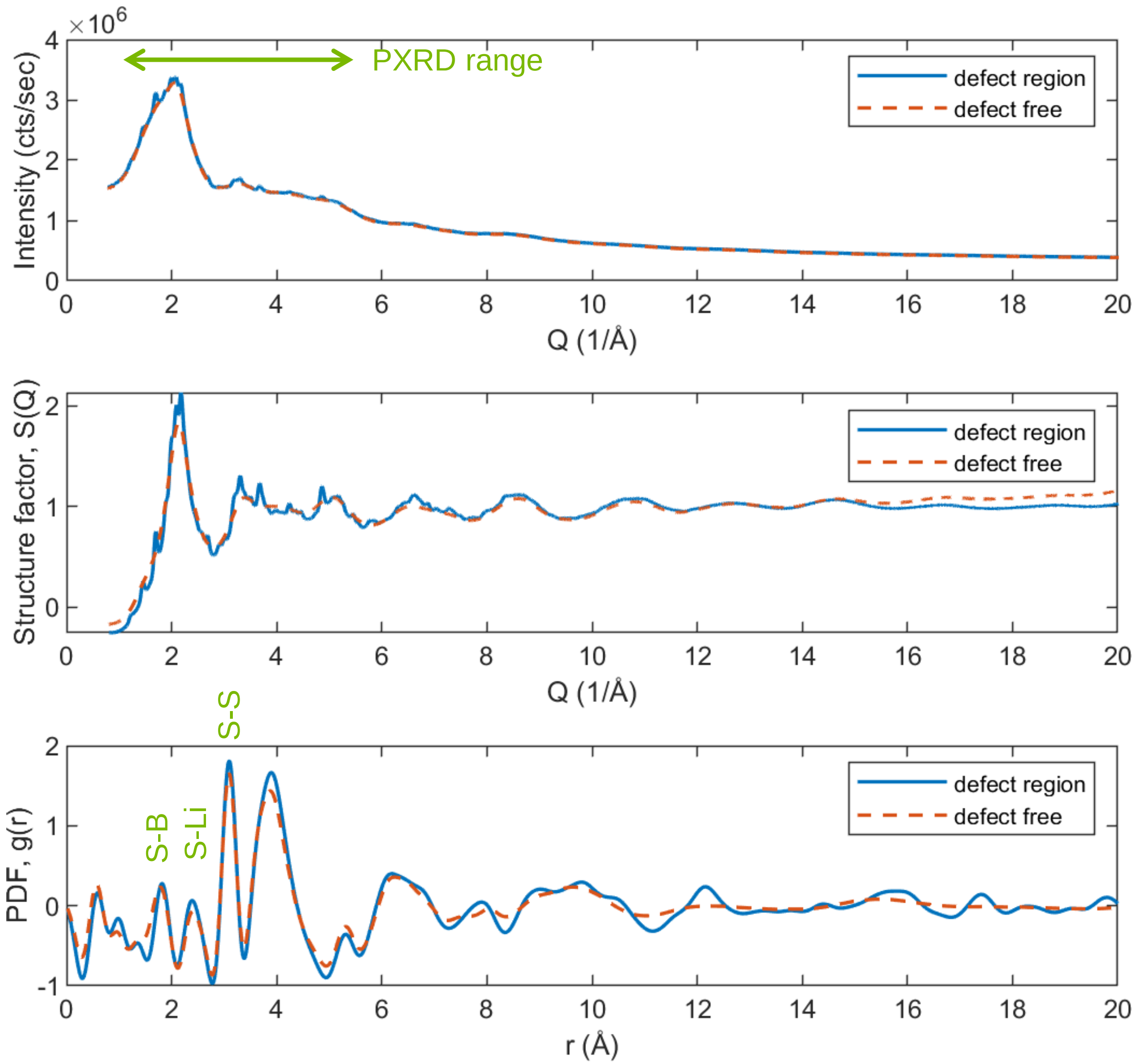
BULK DEFECTS

XRD and Pair Distribution analysis

- Traditional powder diffraction (PXRD): useful for characterizing polycrystalline materials.
  - High Q-resolution/moderate q-range
- Pair distribution function: useful for characterizing noncrystalline materials:
  - Measure to much higher Q
  - Pair correlations related to local structure and does not require long range order



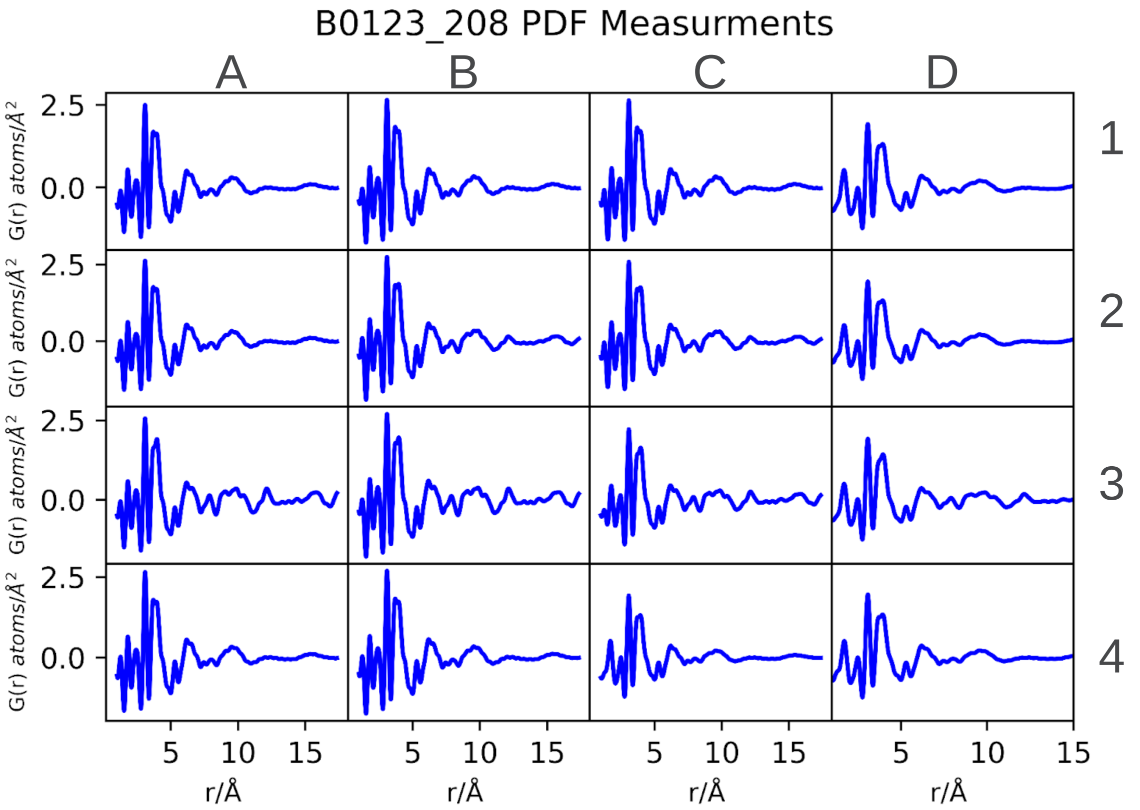
Example: PDF analysis of B0135-208

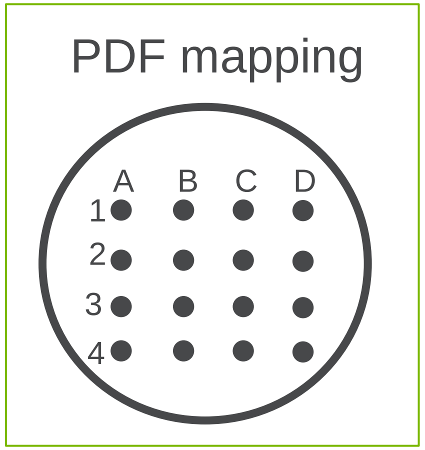


PDF MAPS

Histogram of Atom-Atom distances

- PDF results in all histogram of atom-atom distances in a material.
- Shows structural differences between different regions and samples.
- PDF measurements can take 5-25 minutes.
- Finer scale PXRD maps used to identify regions of interest for PDF.

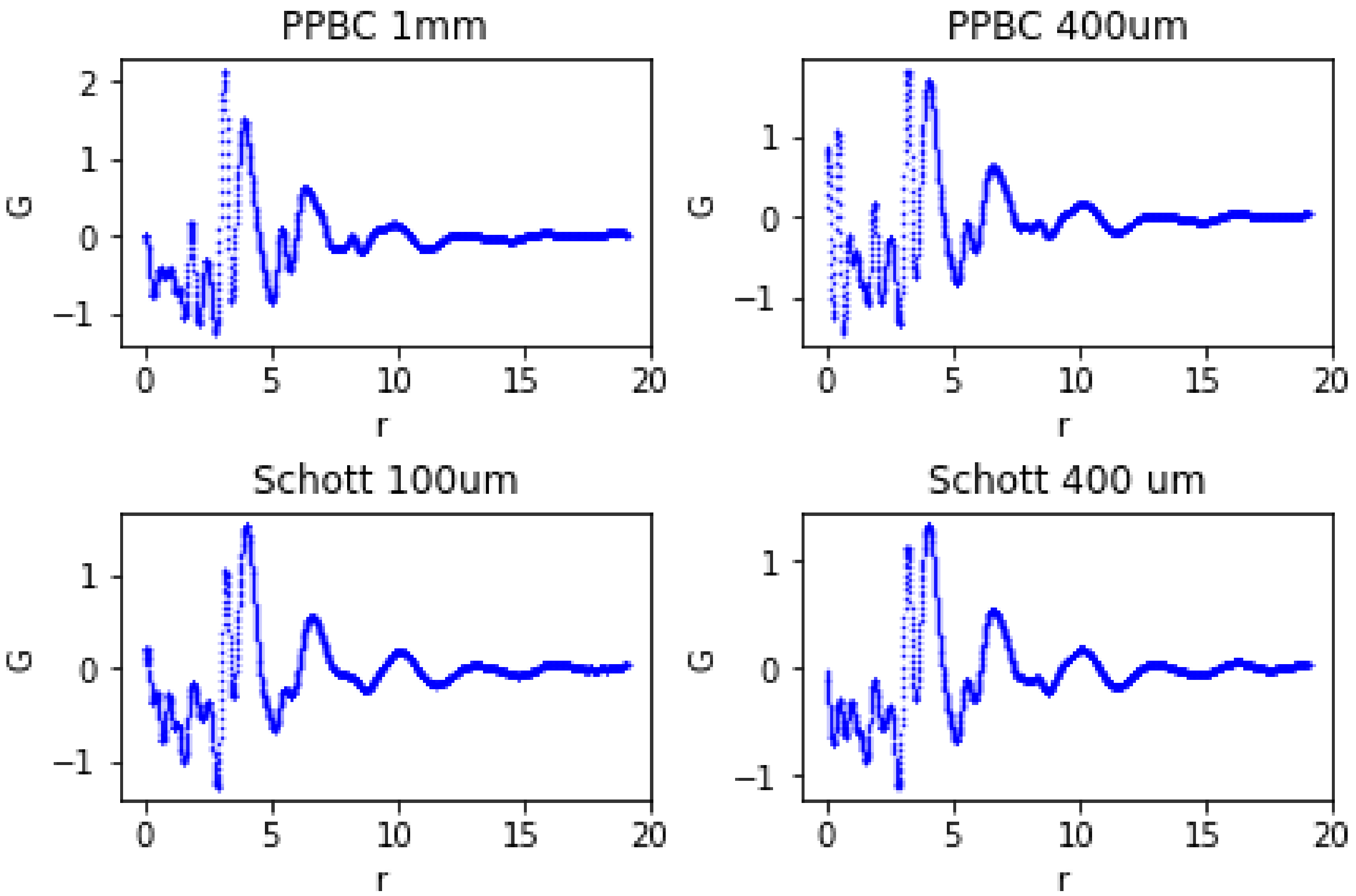




COMPARISON OF SAMPLES

Varying thickness and manufacturer

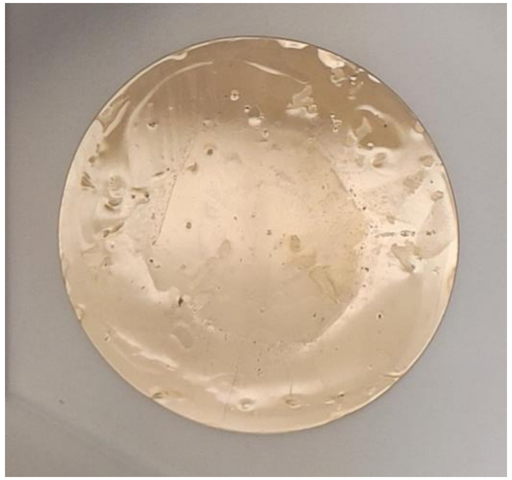
- PDF spectra varies substantially between samples.
  - Variation more pronounced with manufacturer, not thickness.
  - Not surprising give the immature supply chain for sulfide precursors.
  - Currently analyzing PDF from crystallized standards ($Li_xB_yS_z$) to build model for glass structure.

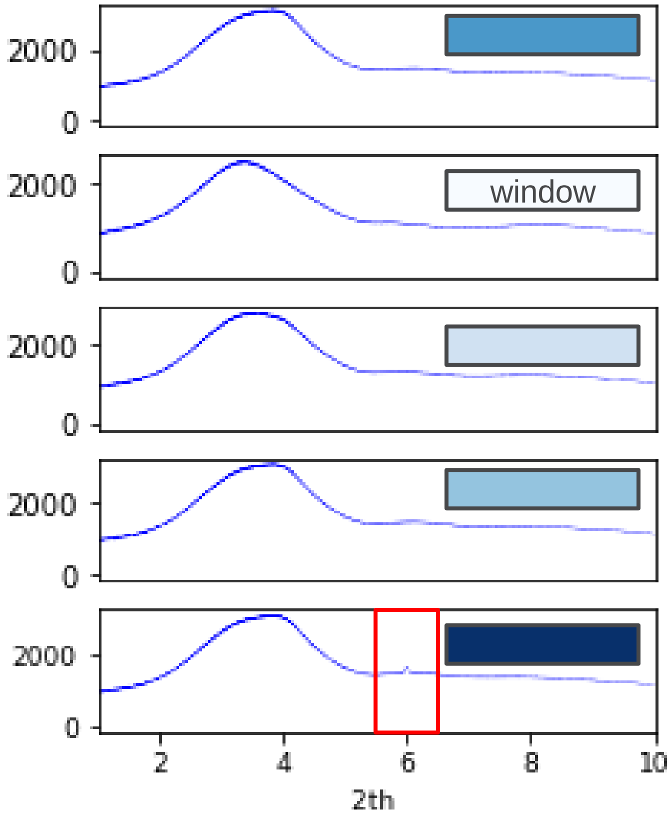


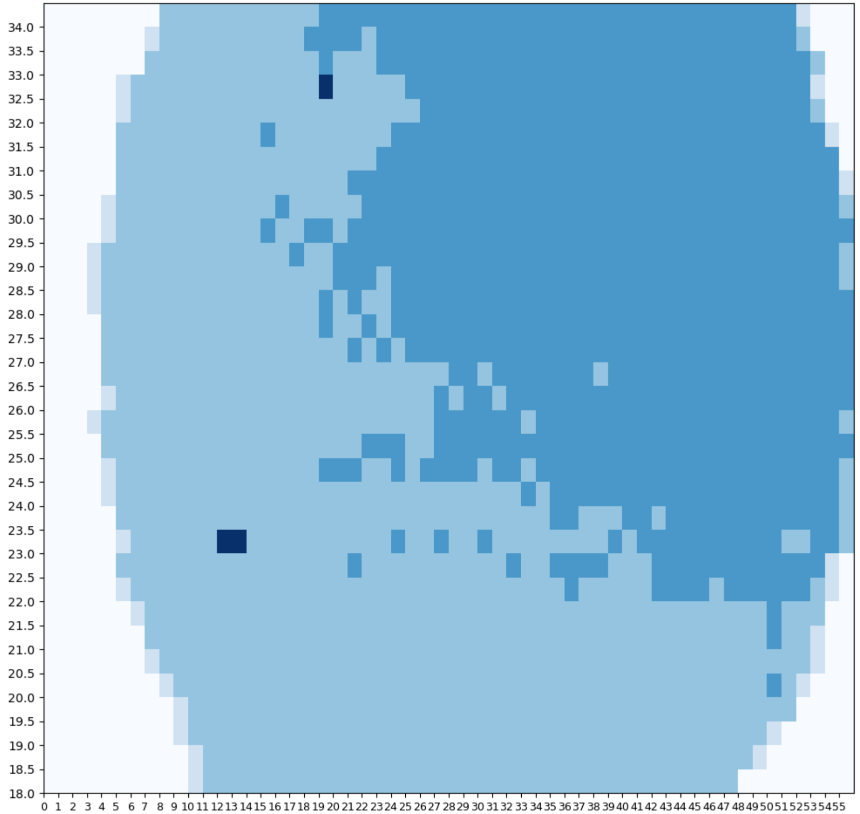
PXRD MAPPING OF CRYSTALLITE INCLUSIONS

K-means clustering approach

- Using an AI approach allows for rapid analysis of the different PXRD regions of the samples.
- Amorphous and crystalline regions can be distinguished.
- Example: B0135-203







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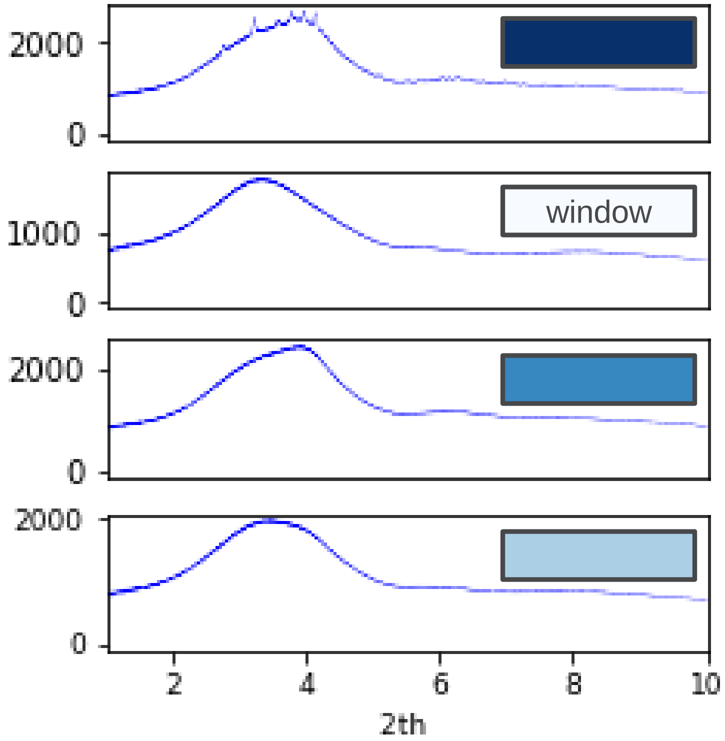
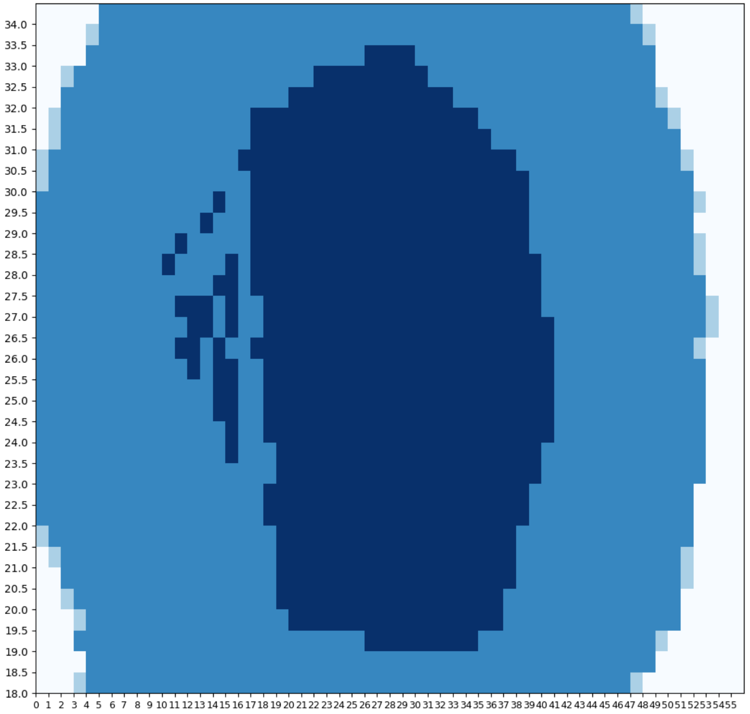
- Example: B0135-208





PXRD MAPPING OF CRYSTALLITE INCLUSIONS

K-means clustering approach

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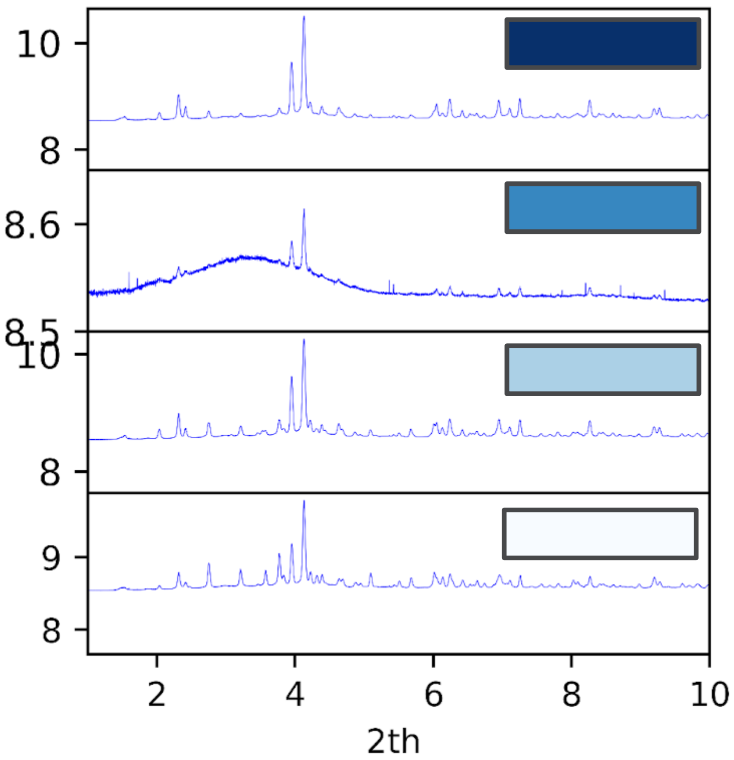
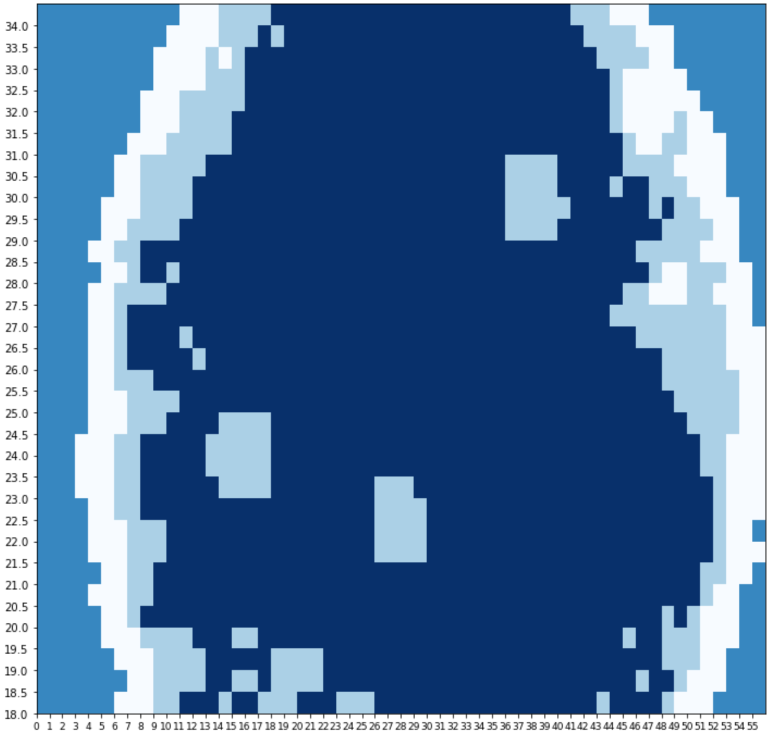
- Amorphous and crystalline regions can be distinguished.
- Example: Intentionally crystallized sample (B0146)

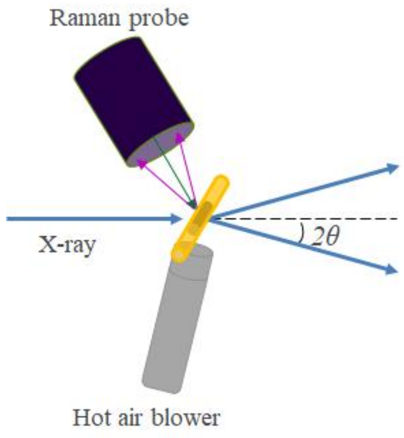


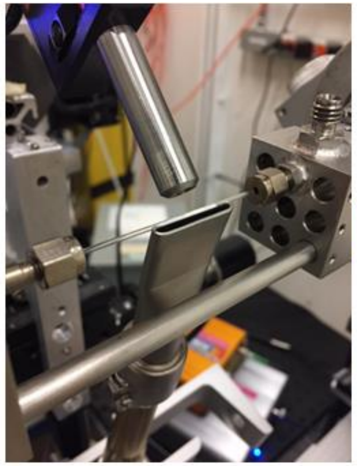


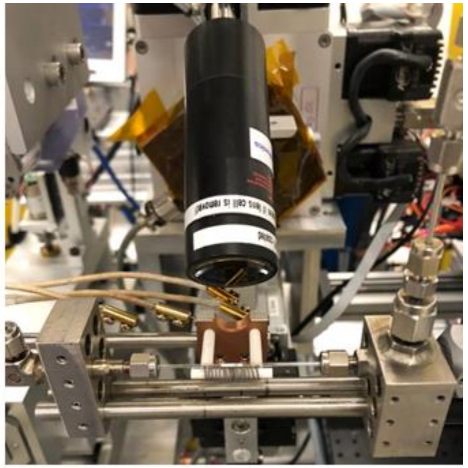
MULTIMODAL APPROACH

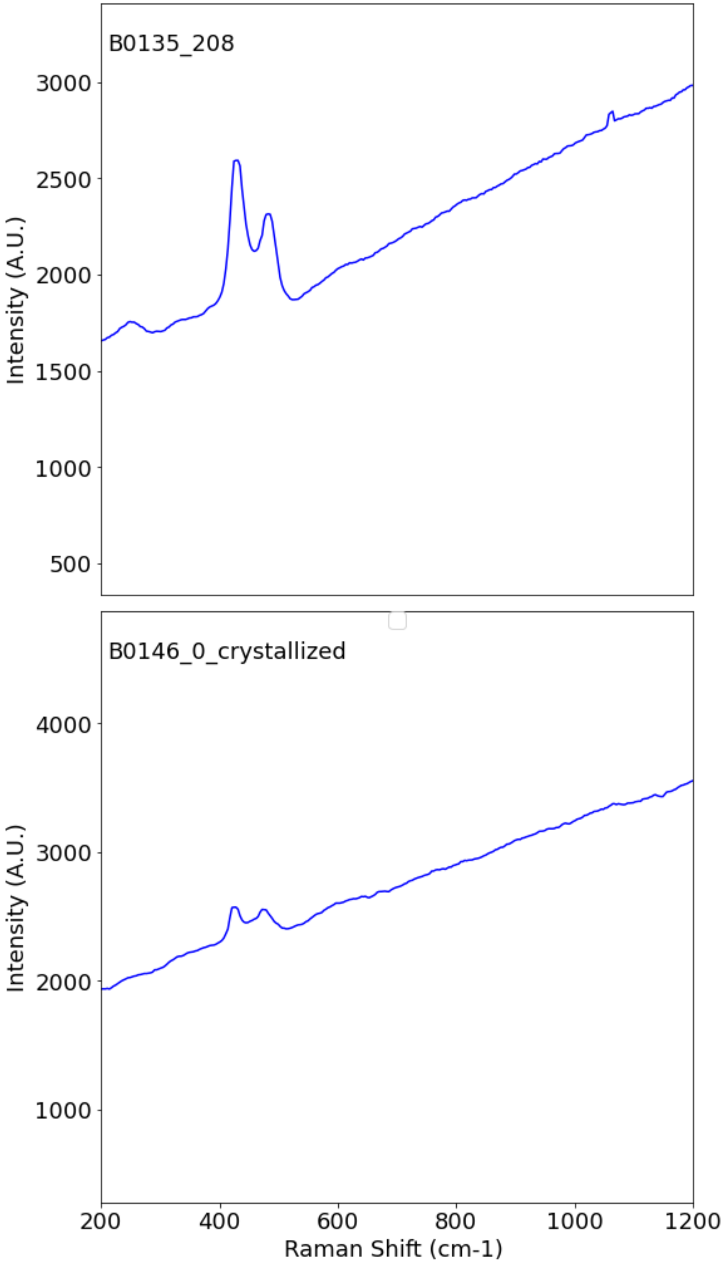
Combining Raman and XRD

- In progress of developing in situ Raman and PXRD measurements for beamline 11-ID-B.
- **Proof of concept:** Initial Raman study of Li-B-S glasses through sample holders.
  - Data is similar to reported $LiBS_2$ glasses
    Tatsumisago, M. et al. *J. Am. Ceram. Soc.*, 71 (9) 766-769 (1988)



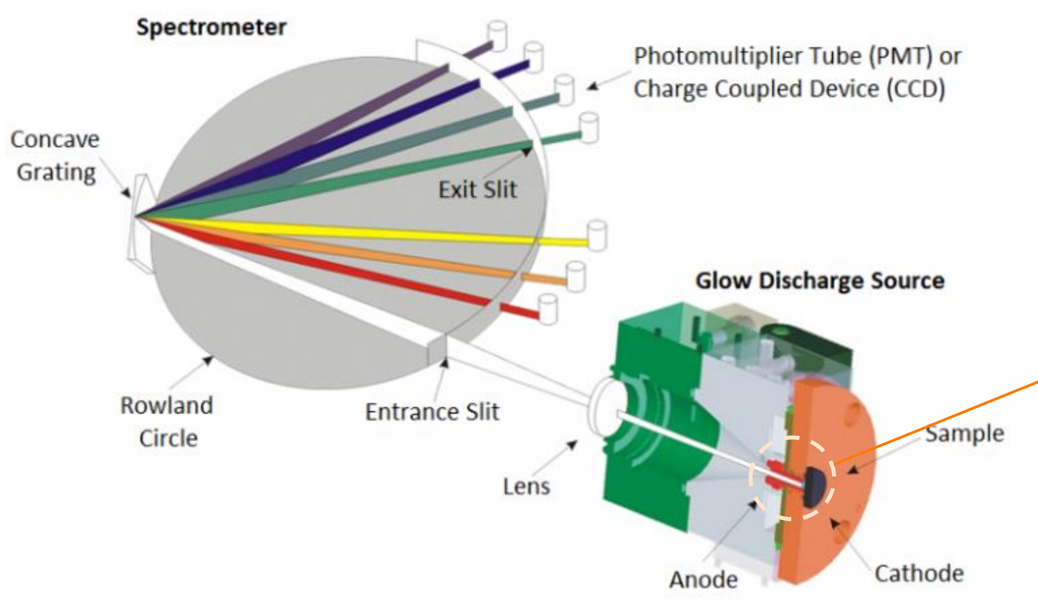


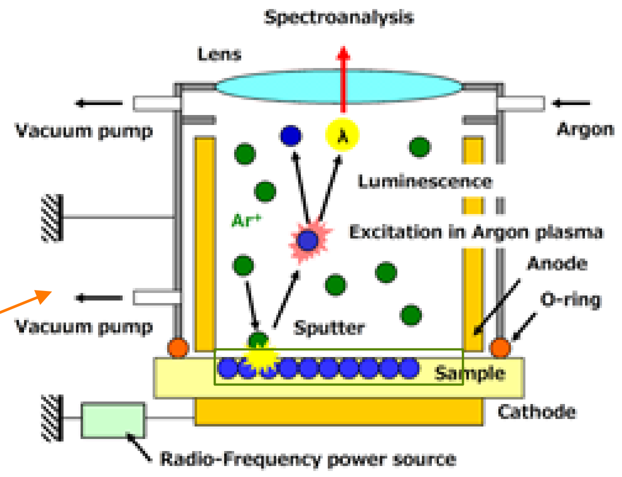




SURFACE/INTERFACIAL DEFECTS

GDOES analysis: Chemical composition depth profiling





Glow discharge optical emission spectroscopy (GDOES)

- Mild plasma → Destructive sputtering → Analysis of elemental emission spectrum.
- Wide range of analytical depth (~nm to ~mm) + Averaged lateral information (4 mm Ǿ).
- Capable of detecting lithium (unlike EDS)
- In principle, quantitative depth profiling with ~2 nm of resolution is possible, if certain prerequisite is met.
  → In this work, qualitative analysis has been done so far.

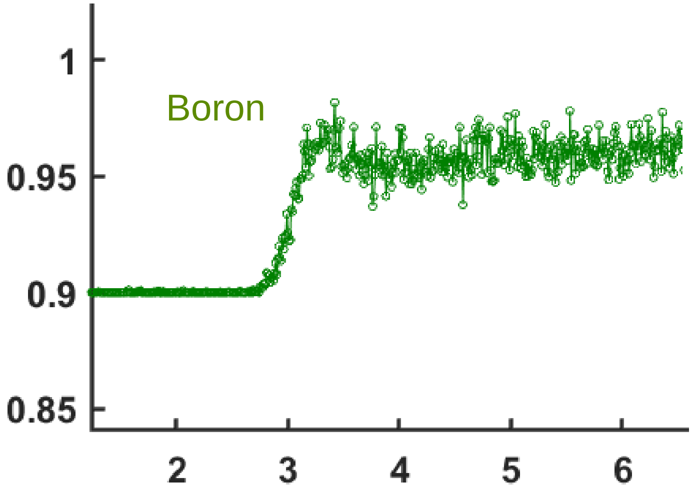
https://www.spectruma.de/en/gdoes-theory.html
https://www.toray-research.co.jp/en/technicaldata/techniques/GD_OES.html

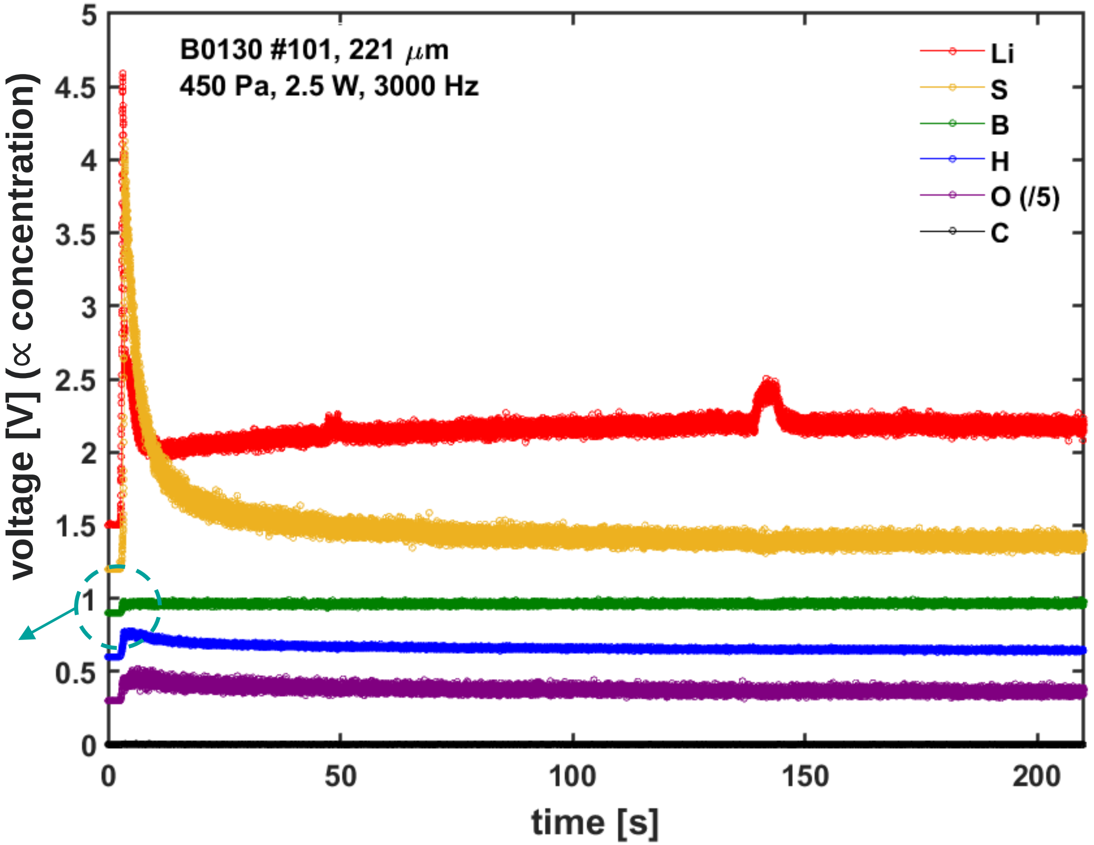
GDOES ANALYSIS

Chemical composition variation – surface *vs.* bulk

At mild sputtering power (2.5 W): probing near surface region.

- Major components - Li, S and B – are present
- Find surface enrichment of Li and S.
- H and O are also present in the glass.
- Local Li rich layer or chunk?



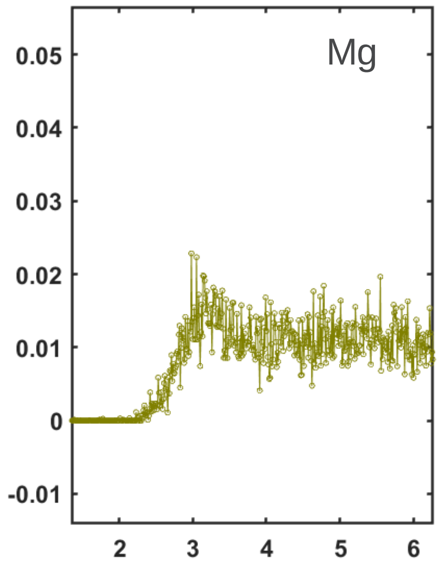


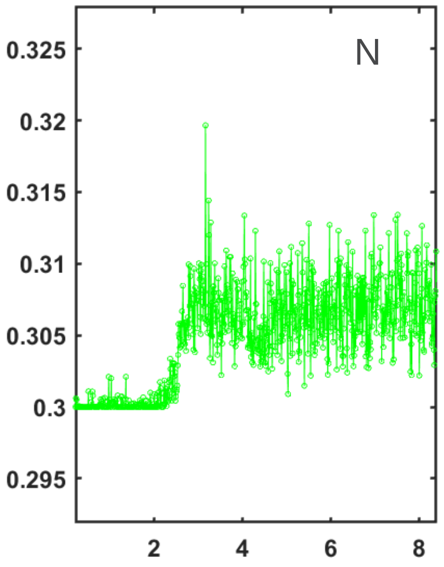
GDOES ANALYSIS

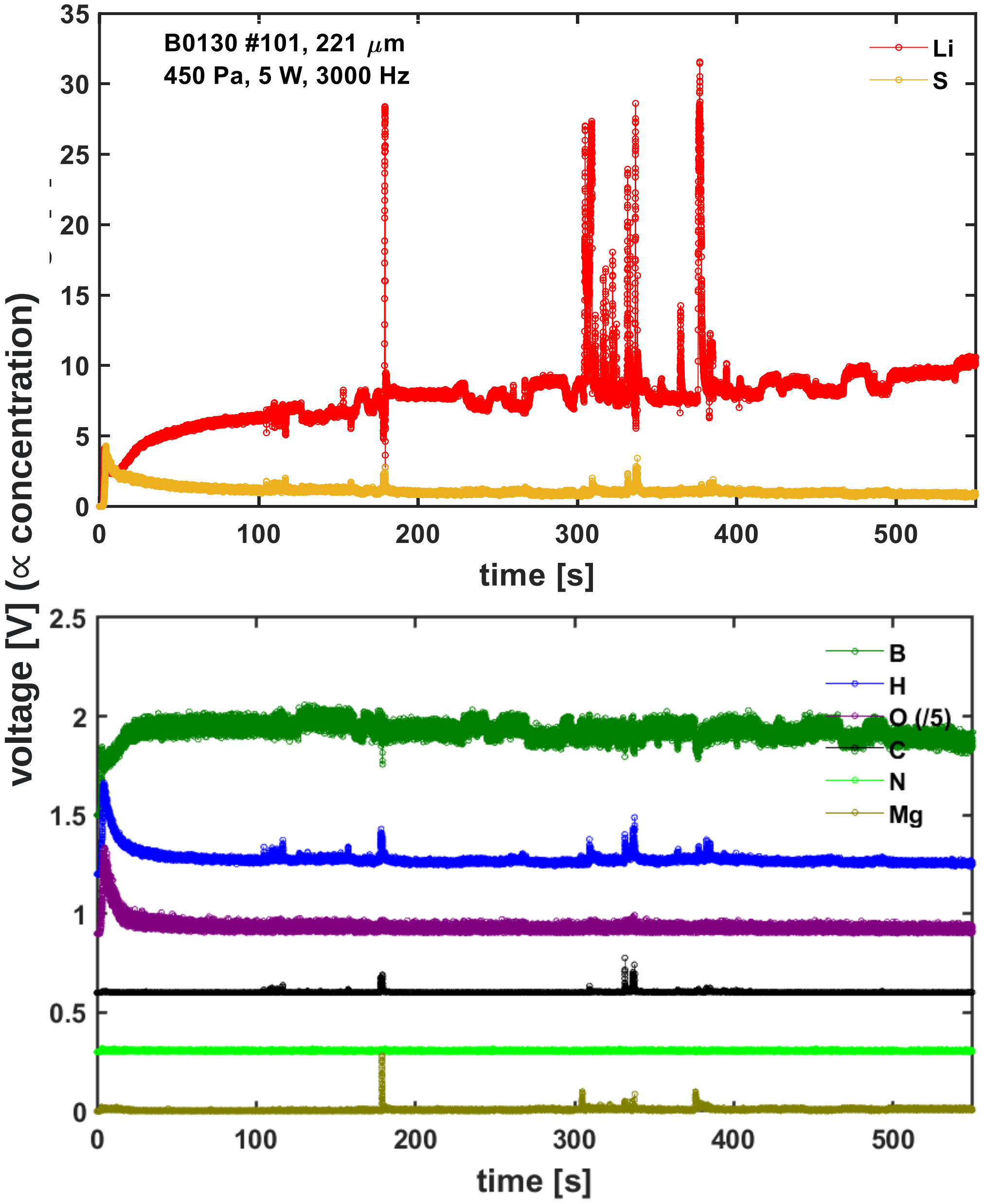
Bulk impurities

At higher sputtering power (5 W), reaching bulk composition.

- Find Mg and N impurities.
- Chemical heterogeneity in bulk.
  - Li, S, H, C, Mg → local segregation.
  - S, H, O → surface enrichment.
  - Li, B → depletion near surface.



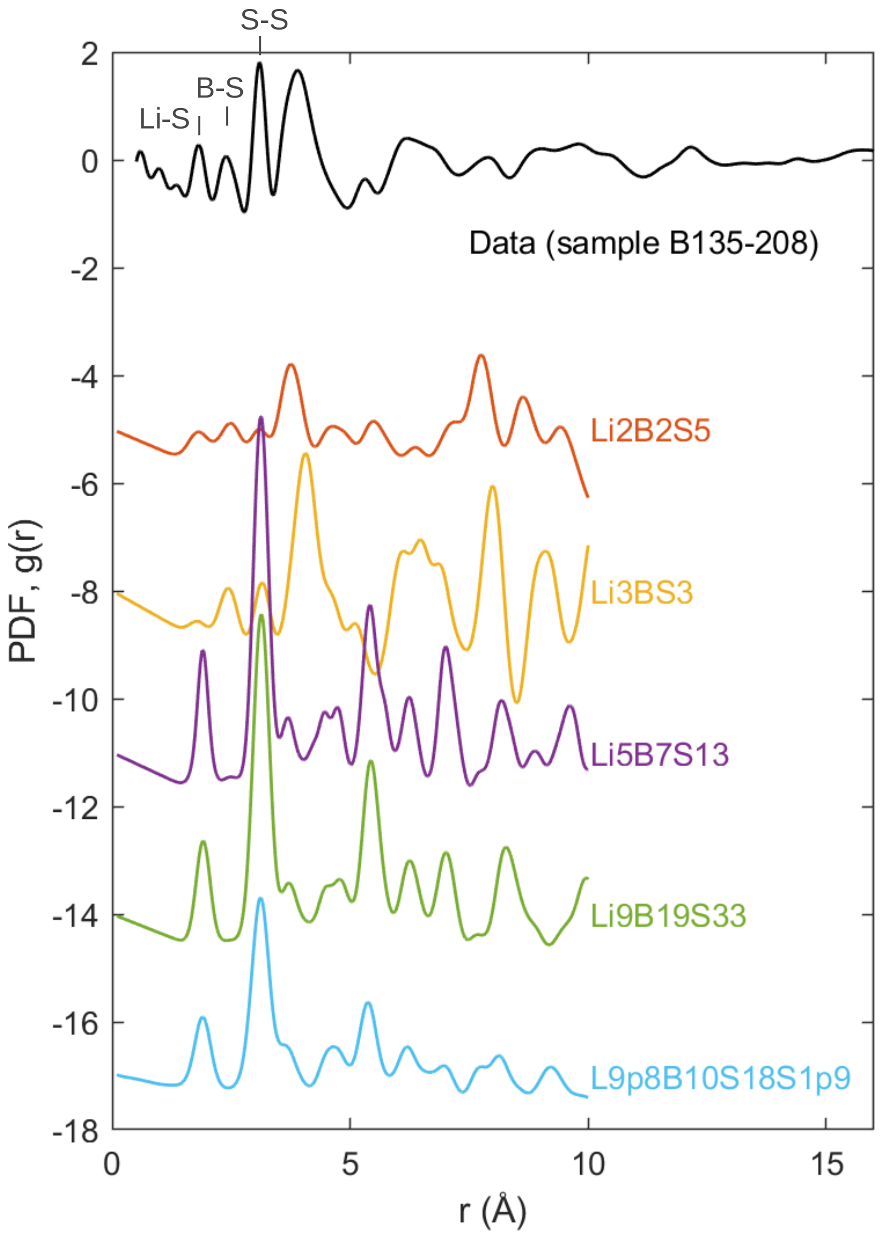




FUTURE WORK

Bulk and interfacial defects

- PDF studies (bulk structure):
  - Incorporate crystalized glass studies (at higher T) to better understand B_xS_y moieties present in glass and structure of crystalline defects (example, right).
  - Compare with Raman spectroscopy at beamline.
- Optical studies (interfacial structure)
  - Calibrate GDOES depth profiling and develop transfer chamber to avoid transient air exposure.
  - Incorporate digital holographic microscopy (DHM) to quantify surface cracking and impurities.
  - Analyze Li/glass interface during cycling by DHM.
- Processing: compare structure of glasses pulled to ~20 µm.



ACCOMPLISHMENTS AND RESULTS

Characterization tools for sulfide glass electrolytes

- Developed routes for characterizing bulk structure of sulfide glass electrolytes ranging from 100-1000 μm thick.
  - Used K-means clustering algorithm to quantify heterogeneity in both crystalline and amorphous species.
- Used SEM and GDOES to study near-surface composition of glass electrolytes.
  - Identified extra species related to processing of glass disks.

Acknowledgements

- Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged (Simon Thompson)